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Subject: <u>QUARTERLY REPORT for Period 8/10-11/10/51</u>
<u>ORNL RaLa and MTR RaLa Process Development</u>

To: <u>F. L. Steahly</u>

From: <u>R. E. Blanco</u>

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                                               Laboratory Section
From: R. E. Blanco

Problem No. TDSI-

Part

QUARTERLY REPORT

Title: ORNL RaLa and MTR RaLa Process Development

Work by: R. E. Blanco, D. M. Helton, A. H. Kibbey, J. F. Land, J. H. Pannell

Secret Notebook No.

SUMMARY

The ORNL RaLa ion exchange purification process was revised to permit the
production of the larger batches now required (30 - 40 kilo-curies). The changes,
listed as follows, were designed to minimize the radiation damage to the system
and decrease the sensitivity of the feed solution to radiation damage: (1)
substitute sodium acetate for Versene as the first feed solution, and (2) in-
crease the flow rates and column size. A full chemical scale tracer level dem-
onstration run showed that the barium yield will be 96% and that the product will
meet purity specifications.

In the MTR RaLa Process, the solubility of uranium in the caustic dissolver
solution and the volume of hydrogen evolved during the dissolution were studied
as a function of aluminum, sodium nitrate, sodium hydroxide, sodium carbonate and
calcium nitrate concentrations. Using the recommended conditions of 5.0M Al,
2.5M NaNO$_3$ and 5.0M NaOH, the uranium solubility was approximately 7 mg/liter
$\approx$ 0.15% uranium loss, and the volume of hydrogen evolved was 9 liters/MTR-assembly.

The separation of barium from uranium and soluble fission products by precipitation of barium nitrate from 85% nitric acid was selected for a process step, rather than the precipitation of barium sulfate from sulfuric acid, because of the solubility of the former in water. The nitric acid precipitation gives a quantitative precipitation of barium nitrate with less than 0.04% uranium loss. The quantitative precipitation of barium sulfate and the amounts of Ce, Sr, U and Al carried by the precipitate were studied.

The MTR RaLa ion exchange flowsheet was revised as follows: (1) A step was added for the selective elution of aluminum with sodium hydroxide; and (2) the flow rates and column size were increased.

The overall barium yield for the MTR RaLa Process was 96% and the product met purity requirements.

The radiation stability of acetate and Versene feed solutions were studied using the 3,000 curie Co^{60} source. The acetate is apparently more stable than the Versene. The former showed no pH change and no barium precipitation after irradiation to 0.160 watt hr/ml, while the pH of the Versene solution changed from 6.3 to 8.5 and 44% of the barium precipitated at 0.143 watt hr/ml.

The Dowex 50 resin capacity loss was determined after the full scale RaLa Run #45 (12,500 curies of Ba^{140}). The results showed that 0.232 K.W.H. of beta radiation/Kg. of oven-dry resin was equivalent to a 20% loss in capacity.

Elution of barium from Dowex 50 was shown to be more efficient with 9M HNO_3 than with 6M or 12M. Contacting Dowex 50 with 12M HNO_3 for 12 hours

showed only a 0.74% capacity loss and 0.17% loss by weight.

1.0 ORNL RaLa Process Development

The ORNL RaLa ion exchange purification process was revised to permit the production of the larger batches now required (30 to 40 kilocuries). RaLa Run #45 at the 20 kilo-curie level demonstrated the instability of Versene after prolonged irradiation at the higher level (see section 5.0). The process changes listed below were designed to minimize the radiation damage to the system and at the same time decrease the sensitivity of the feed solution to radiation damage.

(1) Sodium acetate (0.5M) was substituted in the feed solution for Versene. This solution does not require pH adjustment and the process is not particularly sensitive to any pH change as the result of irradiation. All of the barium is soluble in this solution if the metathesis was complete.

(2) The acetate feed is followed by the regular Versene feed as a tank wash. This solution will require pH adjustment, but the activity level should be low if the metathesis was complete. The Versene will dissolve any barium sulfate remaining in the tanks as a result of a poor metathesis.

(3) The flow rates were increased to 5-8 ml/min/cm^2 column cross-section, as compared to 1.5 in the older process. This results in a decrease in resin and feed solution irradiation time by factors of 4 and 8, respectively. The acetate feed solution passes through the column in ~20 minutes, and the overall process time is ~4.0 hours.

(4)   The column dimensions were changed from 24" x 3" to 18" x 4".
The increased column size permits operation under the non-equilibrium
conditions which result from the use of fast flow rates.

(5)   The concentration of the nitric acid used for the product
elution was increased from 6M to 9M to increase the efficiency of this
operation (see section 3.2).   Experience had shown that the volume of
6M nitric acid needed for complete elution of 10,000 curies of barium
was 4 to 5 times greater than that required on the 1 curie level.   The
increased difficulty in barium elution was undoubtedly the result of
resin irradiation damage.

A full chemical scale tracer level run was made using the new ion
exchange flowsheet and the regular final fuming nitric acid purification
step.   The total barium loss was 4.2%, 3.0% from the ion exchange and
1.2% from the fuming nitric acid precipitation.   The product contained
<10 mg each of Pb, Fe, Cr, Ni and Na, and the Sr and Ce specific acti-
vities were at background level (see flowsheet, Figure 1).

In case of a poor separation of barium from lead in the ion exchange
step, it was of interest to determine the efficiency of their separation
by precipitation from fuming nitric acid.   It was found that the separation
was very poor when the gm concentrations of the lead were less than the
barium.   Under these conditions 99% of the lead coprecipitated with the
barium.   When the lead was in excess, however, the lead solubility was
about 0.22 gm/L of 80% nitric acid.

2.0 MTR RaLa Development

2.1 Solubility of Uranium in the Caustic Dissolver Solution

The solubility of uranium in the caustic dissolver solution was studied as a function of the initial mole ratios of $Al:NaNO_3:NaOH$ and final Al concentrations. Representative results were plotted as a function of total ionic strength as a convenient method for the presentation of several variables. It was assumed that the only cation present was sodium and that all of the ions were monovalent. The solutions were neutralized with acid prior to analysis to dissolve any solids. The additional dilution lowered the uranium concentration to ~ 1 microgram/ml, or less, resulting in an analytical accuracy of $\sim 10\%$. The uranium solubility varied indirectly with the $NaNO_3$ concentration and directly with the NaOH concentration at constant Al concentration; and indirectly with Al concentration at constant $NaNO_3$ and NaOH concentrations (see Figure 2).

The selection of flowsheet dissolver conditions as mole ratios of $Al:NaNO_3:NaOH$ of 1:0.5:1 at 5.0 M Al, was based on uranium solubility and solution stability. Under these conditions the U loss in the dissolver filtrate should approximate 0.15% ($\simeq 184$ mg U 235).

The effect of $CO_3^=$ and Ca^{+2} on the solubility of uranium was studied. Dissolver solutions which were made up to 0.3M in $CO_3^=$ or up to 0.07M in Ca^{+2} did not show any appreciable difference in uranium solubility from normal solutions.

2.2 Dissolver Off-Gas (MTR Falor)

The evolution of hydrogen during the caustic dissolution was studied and plotted using the same variables and assumptions as those listed for uranium solubility in Section 2.1. It was found that the volume of hydrogen off-gas varied directly with the initial NaOH concentration at constant Al and $NaNO_3$ concentrations; and indirectly with the initial $NaNO_3$ concentration at constant Al and NaOH concentrations. At the recommended flowsheet conditions of mole ratios of 1:0.5:1 at 5.0M Al, the hydrogen evolution did not exceed 2 ml/gm of MTR-Assembly (see Figure 3).

The following two equations describe the dissolution of aluminum in caustic and sodium nitrate:

$$8Al + 5\ NaOH + 3\ NaNO_3 + 2H_2O \longrightarrow 3NH_3 + 8\ NaAlO_2 \qquad (1)$$

$$2\ Al + 3\ NaNO_3 + 2\ NaOH \longrightarrow 3\ NaNO_2 + 2\ NaAlO_2 + H_2O \qquad (2)$$

A plot of the ratio of the final concentrations of $\frac{NO_2^-}{Al}$ shows that the fraction of the aluminum dissolved by equation (2) varies directly with increasing initial $NaNO_3$ concentration at constant Al and NaOH concentrations; and indirectly with increasing initial NaOH concentration at constant Al and $NaNO_3$ concentrations. In plotting the percent of aluminum dissolved by equation (2), it was assumed that the ratio of the rate of production of NO_2^- to the rate of Al dissolution was constant throughout the dissolving period (see figure 4).

2.3 Separation of Barium and Uranium

2.31 Fuming Nitric Acid Precipitation

It had been planned to separate the barium from the uranium and sulfate soluble fission products by the precipitation of $BaSO_4$. The precipitate was to be dissolved in Versene for further purification by ion exchange. This scheme has been abandoned as the result of the radiation instability of Versene in favor of the precipitation of $Ba(NO_3)_2$ from fuming nitric acid. The advantages of the nitric acid precipitation are: (1) the high solubility of $Ba(NO_3)_2$ in water, (2) the improved separation of barium from the rare earths, and (3) the decrease in corrosion. A disadvantage is the decrease in separation of barium from aluminum and strontium.

A fuming nitric acid precipitation was performed using the expected process conditions. In this case the precipitate had the following composition, based on the total of each component in the system:

Barium	- -	99.6%
Strontium	-	99.1%
Cerium	=	4.7%
Aluminum	=	0.23%
Uranium	-	0.04% (see flowsheet, Figure 5)

2.32 Sulfuric Acid Precipitation

The quantitative precipitation of $BaSO_4$ and the amounts of Ce, Sr, U and Al carried by the precipitate under the anticipated process conditions were studied as a function of Ba, HNO_3 and H_2SO_4 concentrations, digestion conditions and temperature.

The results, plotted in Figures 7, 8 and 9 showed the following: (1) the barium loss in the filtrate increased with HNO_3 concentration and temperature, and decreased with increasing H_2SO_4 concentration; (2) the amounts of Ce, Sr, Al and U carried by the $BaSO_4$ increased with the concentrations of HNO_3, H_2SO_4 or Ba, reaching maximums of 12%, 80%, 45% and 0.15%, respectively.

2.4 Purification of Barium by Ion Exchange

The previously published flowsheet was revised as follows:

(1) Sodium nitrate (0.5M) was used instead of Versene to dissolve the barium precipitate and form the feed to the ion exchange column. Sodium nitrate was used rather than water in order to hold the resin column in the sodium form. The solution will contain residual acid from the precipitation tank which would convert the column to the H+ form.

(2) An additional step was added for the selective elution of aluminum with dilute sodium hydroxide.

(3) The column size was increased from 4" x 7" to 4" x 10".

(4) The flow rates were increased from 1.5 to 5-8 ml/min/cm² column cross-section (see Figure 6).

3.0 Elution of Barium from Dowex-50 Resin with Nitric Acid

3.1 Stability of Dowex-50 Resin in Nitric Acid

The stability of Dowex-50 resin was studied in 6M, 9M, and 12M nitric acid to determine the practicality of barium elution under these conditions. About 20 gm of clean resin was shaken for 24 hours with 75 ml of nitric acid,

the phases separated by filtration, and the filtrate analyzed for sulfate and total solids. The resin was washed with water and its capacity determined by titration with 0.1M sodium hydroxide. At the same time, the moisture content was determined by weight loss in a 105°C oven, and the final capacity results reported on an oven-dry basis.

The results showed that the resin is quite stable even in 12M nitric acid, where the capacity loss was 0.74% as determined by the solution sulfate analysis. This analysis is considered more accurate than the titration method which showed a capacity loss of zero. The C.P. resin was apparently more stable than the technical grade and there was no appreciable difference in the stability of the 8% and 12% cross-linked technical grades of resin (see Table 1).

3.2 Elution of Barium with Nitric Acid

The relative efficiencies of 6M, 9M, and 12M nitric acid were determined for the elution of barium from a Dowex 50 resin column. Batch equilibrations had shown Ba distribution coefficients of 1.0 and 0.5, respectively, for 6M and 9M. It was expected that 12M nitric acid would be even more favorable as a result of its higher H+ concentration and activity coefficient. The column runs showed, however, that the 9M acid was only about 20% more efficient, and the 12M actually less efficient than the 6M acid (see figure 10). A possible explanation of this phenomenon would be the precipitation of barium nitrate in the resin particles at the high H+ concentrations encountered in the interior

of the resin particles as a summation of the $H^+_{HNO_3} + H^+_{SO_3H}$. The flat appearance of the elution curve suggests the redissolution of a precipitate.

4.0 Physical and Chemical Characteristics of Dowex-50 Resin

Standard procedures were set up for the determination of the physical and chemical characteristics of Dowex 50. These tests can be used for resin evaluation on receipt and during processing. The determinations include capacity, moisture content, cross-linkage, swelling coefficient and separation efficiency.

5.0 Radiation Stability of Dowex-50 Resin

All of the feed and effluent solutions from RaLa Run #45 were analyzed for Ba, Sr, Ce and gross β. Using these analyses, it was possible to calculate the average residence time of the activity on the column and therefore the total β energy absorbed by the column system. It was assumed that the gamma radiation damage was negligible and that the beta damage was proportional to

$$E_{(average)} = (0.4)E_{(maximum)}$$

(Rev. Mod. Physics, 19, 25(1947)

The calculations showed that processing 12,500 curies of Ba^{140}, 1,740 curies of Sr^{89}, 500 curies of La^{140} and 528 curies of $Ce^{141, 144}$, subjected the resin column to 0.232 K.W.H. of radiation energy/Kg of oven dry resin or 0.112 K.W.H./ liter of H^+ resin. The resin loss in capacity was 20%. The loss in capacity was determined by passing excess standard acid through the sodium form column both before and after the run. The amount of acid retained by the column is

equal to its capacity.

The loss in capacity by the resin column did not impair the efficiency of the system for Ba purification. It is therefore assumed that the ion exchange column will be suitable for purifications at the proposed higher levels since the irradiation time in the new flowsheet is lower by a factor of 4, as compared to the proposed radiation level increase by a factor of 3.

6.0 Radiation Stability of Versene and Acetate

RaLa production Run #45 was at the 20 kilocurie level. Under these conditions it was found that the Versene in the feed solution was slowly decomposed with a resultant rise in pH at a rate of 0.4 - 0.6 unit per hour. In addition, after a total average irradiation of $\sim$ 13.5 hrs. $\approx$ 0.0404 watt hr/ml, about 35% of the barium was precipitated, either as an organic salt or as barium sulfate.

Synthetic RaLa feed solutions of Versene and acetate, free from sulfate, were irradiated in the 3,000 curie Cobalt[60] source to study their radiation stability in detail. The results show that the acetate feed is much more stable than the Versene feed. The former solution showed no barium, strontium, cerium or lead precipitation at 0.160 watt hr/ml, which is a factor of 18 higher than the radiation expected from 35 kilo-curies of barium[140] using the new flowsheet. The pH rose from 4.92 to 5.13. Since the final solution was not analyzed for acetate, it is not known whether the small pH rise indicates that (1) the acetate is more stable to radiation than Versene, or that (2) the high concentration of acetate buffer prevents any pH charge. In addition the organic salts

of the cations, or their hydroxides and carbonates in the case of lead and cerium, would be less likely to precipitate at pH 5.0 than in the range of 6.0 - 8.0. It was shown that Fe, Cr and Ni do not act as protective agents against radiation damage. Radiation of the Versene solution showed a progressive decomposition of the Versene with a resultant precipitation of the Ba, Sr, and Ce. Barium precipitation was 0%, 44% and 98.4%, respectively, at radiation levels of 0.0518, 0.143, and 0.155 watt hr./ml. Lead precipitation was negligible at the highest radiation, indicating that at least 1/2 of the Versene remained undamaged at this point. It is assumed that the presence of sulfate accounts for the 35% precipitation of barium in the process solution at 0.0404 watt hr/ml versus zero precipitation in the synthetic at 0.0518 watt hr/ml. Bromide was tried as a radiation protective agent, as suggested by Hochanadel and Ghormley, and shown to be unsatisfactory. Other radiation effects on the Versene solution are listed as follows:

(1) The NO_2^- increased from 0 to 0.125M.

(2) The total N remained constant.

(3) The ability to chelate Ca^{+2} disappeared.

(4) The pH rose from 6.25 to 8.5.

(5) The solution color changed from white to yellow.

(6) The irradiated solution 34% more acid to decrease the pH from 10.8 to 6.3 as did the original. This indicates the formation of additional weak acid and/or amino groups. The titration curve was much flatter for the irradiated sample in the pH range 7.5 to 6.3. This work is summarized in Table 2.

Table 1

Stability of Dowex 50 Resin in Aqueous Nitric Acid Solutions

Conditions:

20 gm (oven-dry) resin shaken for 24 hours with 75 ml HNO_3

Phases separated by filtration through #42 Whatman Paper, filtrate analyzed for $SO_4^{=}$ and total solids.

Resin washed with deionized H_2O, and capacity determined by titration with 0.1M NaOH.

Resin Sample	Capacity - MEQ/Gm (Oven-Dry)				*$SO_4^{=}$ leached out - % of total present in Resin			Total Solids in HNO_3 % of Resin wt. (Oven-Dry)		
	Original	HNO_3 Concentration			HNO_3 Concentration			HNO_3 Concentration		
		6M	9M	12M	6M	9M	12M	6M	9M	12M
L-2566-11 (C.P. - 12% Cross-Linked)	5.08	5.10	5.10	5.12	0.03	0.03	0.03	-	-	-
L-2647-28 (Tech.-12% Cross-Linked)	5.01	4.95	4.97	4.97	0.19	0.51	0.74	0.07	0.17	0.17
L-2566-47 (Tech.-8% Cross-Linked)	5.03	5.12	5.14	5.13	0.14	0.34	0.50	--	--	--

* Equivalent to % resin capacity loss.

Table 2

Study of the Radiation Stability of Versene and Acetate RaLa Feed Solutions

Versene Feed:

$0.44M\ NO_3^-$
$0.065M$ Versene $0.0009M$ Ba
$0.018M$ Fe(3), Specific $0.03M$ Pb $0.0015M$ Sr
$0.1N$ Na Br (Run V-3, only)
Sp. gr. = 1.0

Acetate Feed:

$0.49M$ Na Acetate $0.072M$ Pb
$0.1M\ NO_3^-$ $0.0018M$ Fe   (Runs Na-Ac-
$0.0029M$ Ba $0.00058M$ Ni   1 to 3, only)
$0.0046M$ Sr $0.00033M$ Cr
     Sp. gr. = 1.02

Ba^{140}, Sr^{90} and Ce^{144} Tracer

Source: 3,000 curies (Co^{60}) = 2.16×10^{-3} watts/gm. solution

Procedure: Irradiate at atm. pressure in equilibrium with air; filter through #42 Whatman paper. Analyze filtrate and precipitate.

Run No.	Irrad. Time (Hours)	Total Irradiation (Watt Hrs/ml.soln)	pH Initial	pH Final	NO_2^- Formed (M)	Final *Versene Conc.(M)	% of Total Precipitated Ba	Sr	Ce	Pb
V-1	66.5	0.143	6.30	8.50	0.125	0	44	25.2	58	0
V-2	24	0.052	6.11	8.53	0.018	0.014	0	0	~1.6	0
V-3	72	0.155	6.30	8.05	0.119	0	98.4	98.4	99.6	0
Na-Ac-1	47	0.103	4.92	5.03	0.0087	-	0	-	--	0
Na-Ac-2	24	0.053	"	5.00	0.0045	-	0	-	--	0
Na-Ac-3	74	0.163	"	5.13	0.0072	-	0	0	0	0
Na-Ac-4	24	0.053	5.00	5.08	0.0048	-	0	0	0	0
Na-Ac-5	**72.8	**0.160	"	5.18	0.0114	-	0	0	0	0

* Free versene - i.e. not complexed by the Pb
** Corrected to correspond with the other data; actual irradiation was 91 hours at 0.8 regular activity level.

Figure 1

FLOWSHEET: REVISED ORNL - RaLa ION EXCHANGE PROCESS

Figure 1

CRUDE PRODUCT ADSORPTION
Ba = 100-150 gm
Sr,Ce =100;
.5M Na Acetate [per leach]
10.0 L

H_2O
?.0 Liters

LEAD ELUTION
1.5M NaOH
17.0 L

H_2O
10.0 L

VERSENE FEED
0.0625 M
Na Versenate
pH 6.0 - 6.3
15.0 L

H_2O
2.0 L

STRONTIUM ELUTION
0.07M
Na Versenate
pH 6.3
3.4 L

H_2O
7.5 L

SODIUM ELUTION
1.0M HCl
15.0 L

H_2O
4.0 L

PRODUCT ELUTION
9.0 M HNO_3
17.0 L

PRODUCT PRECIPITATION
91% HNO_3
6.0 L

WASH
85% HNO_3
1.0 L

PRECIPITATE DISSOLUTION
HCl
H_2O
0.35 Liters

ION EXCHANGE COLUMN
DOWEX-50, Na^+ RESIN
60 - 100 Mesh - 4" Dia. x 19"

EVAPORATOR
Ba = 97%   Pb = <17.0 mg
Sr = ~0.8;   Na = 1.5 gm
Ce = 38.6%   Fe,Ni + Cr=0.25 g
Evaporate to 2.0 L

85% HNO_3
8.0 L

To Shipping Conc

Filter

LEACH WASTE
Ba = 0;
Sr = 0;
Ce = 2.8%
15.0 L

LEAD WASTE
Ba = 0;
Sr = ~1%;
Ce = 12.0%;
27.0 L

VERSENE WASTE
Ba = 1.2;
Sr = ~80%;
Ce = 37.8%
18.0 L

STRONTIUM WASTE
Ba = 0.9;
Sr = ~1;
Ce = 7.6;
10.0 L

SODIUM WASTE
Ba = 0.7;
Sr = <0.04;
Ce = ~1.0;
19.0 L

NITRIC ACID WASTE
Ba = 1.2;
Sr = ~0.1;
Ce = ~37.2;
Pb = ~16.0 mg
Na = ~1.36 g
Fe,Ni,Cr=~230 mg

PRODUCT ANALYSIS
Ba = 95.8;
Sr = ~0.7;
Ce = <1.6;
Pb = <1.1 mg
Na = 0.14 g
Fe,Na,Cr = <10 mg Each

DWG. No 12793

Figure 2

URANIUM SOLUBILITY AS A FUNCTION OF TOTAL IONIC STRENGTH

CONDITIONS: Approximately 20 gm transverse sections of an MTR-Assembly were dissolved in $NaNO_3$ - NaOH solution.

KEY : Initial mole ratios are indicated as Al: $NaNO_3$: NaOH; Al molarity = final concentration.

ASSUMPTIONS : Final Solution: (1) Na^+ is the only cation.

(2) All anions are monovalent.

(3) Total ionic strength $\approx$ (Na) x 2

JEF

Figure 3
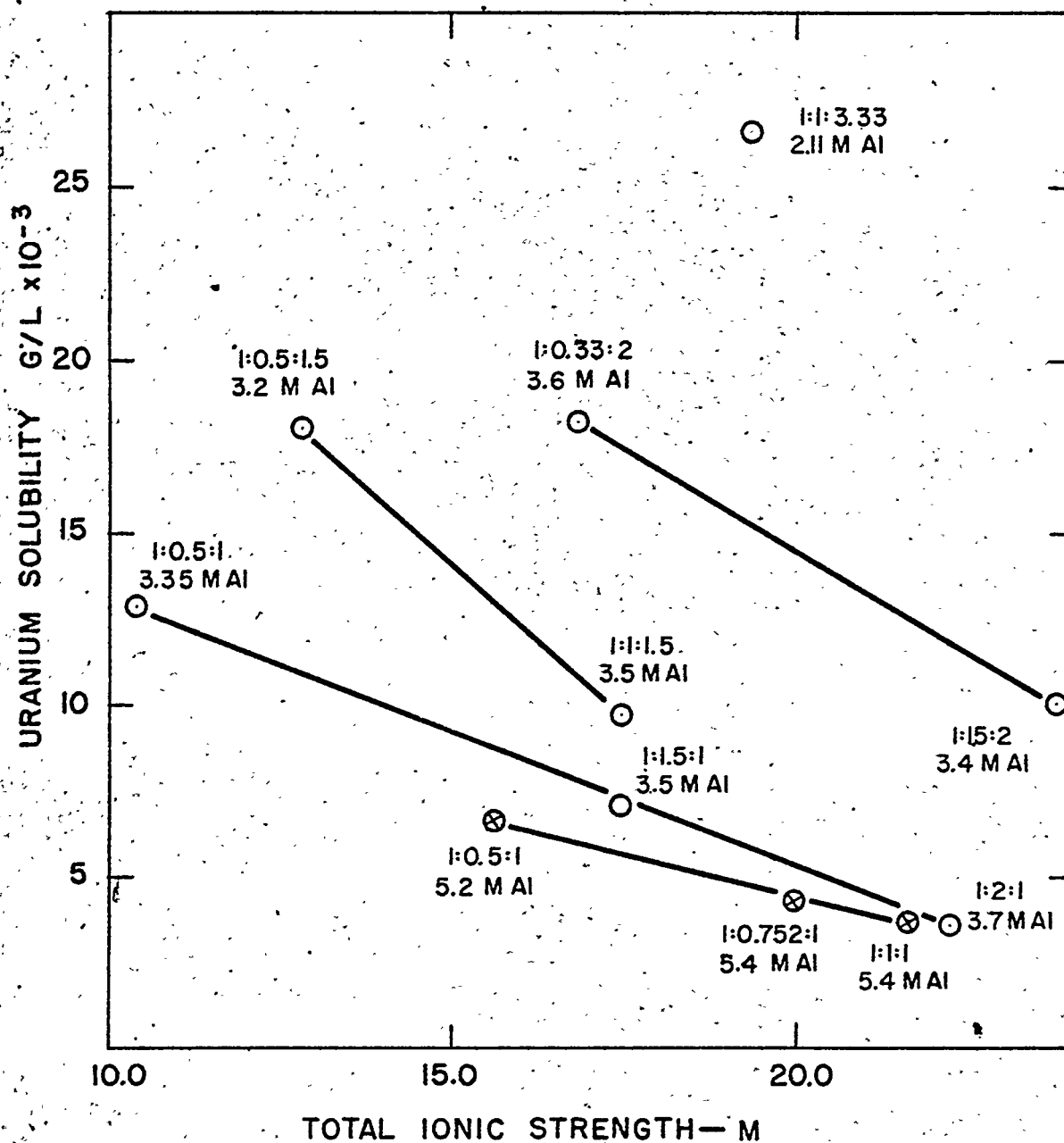
HYDROGEN EVOLUTION AS A FUNCTION OF TOTAL IONIC STRENGTH

CONDITIONS: Approximately 20 gm tranverse sections of an MTR-Assembly were dissolved in $NaNO_3$ — NaOH solution. Off gas was collected and analyzed.

KEY: Initial mole ratios are given as Al: $NaNO_3$: NaOH; Al molarity = final concentration.

ASSUMPTIONS: Final Solution: (1) Na^+ is the only cation.
(2) All anions are monovalent.
(3) Total Ionic strength $\approx$ (Na) x2

LEGEND:

—————— Function of (NaOH); (Al) and ($NaNO_3$) constant.
— — — Function of ($NaNO_3$); (Al) and (NaOH)   ,,
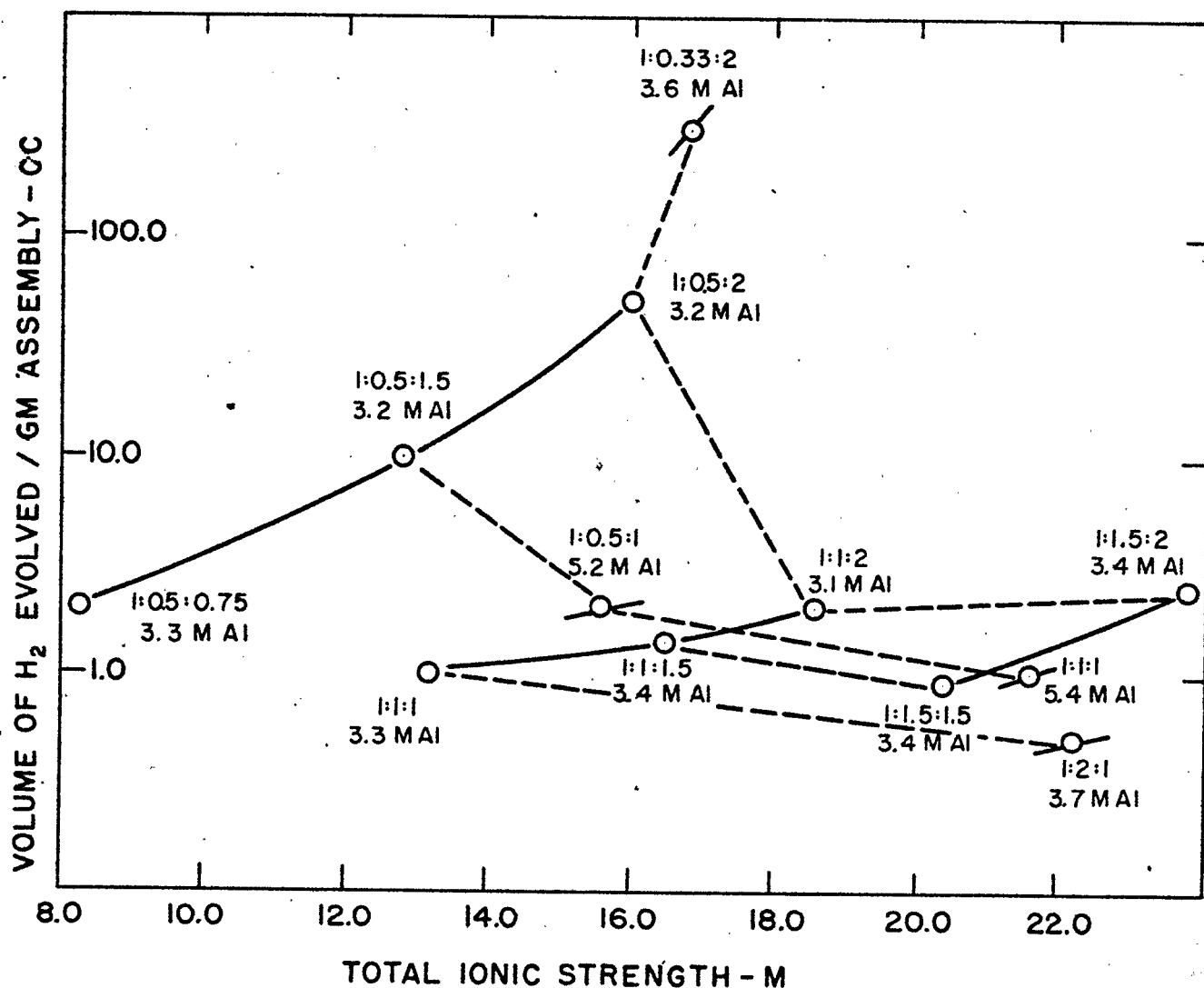
RATIO OF FINAL NITRITE CONCENTRATION TO ALUMINUM CONCENTRATION AS A FUNCTION OF TOTAL IONIC STRENGTH
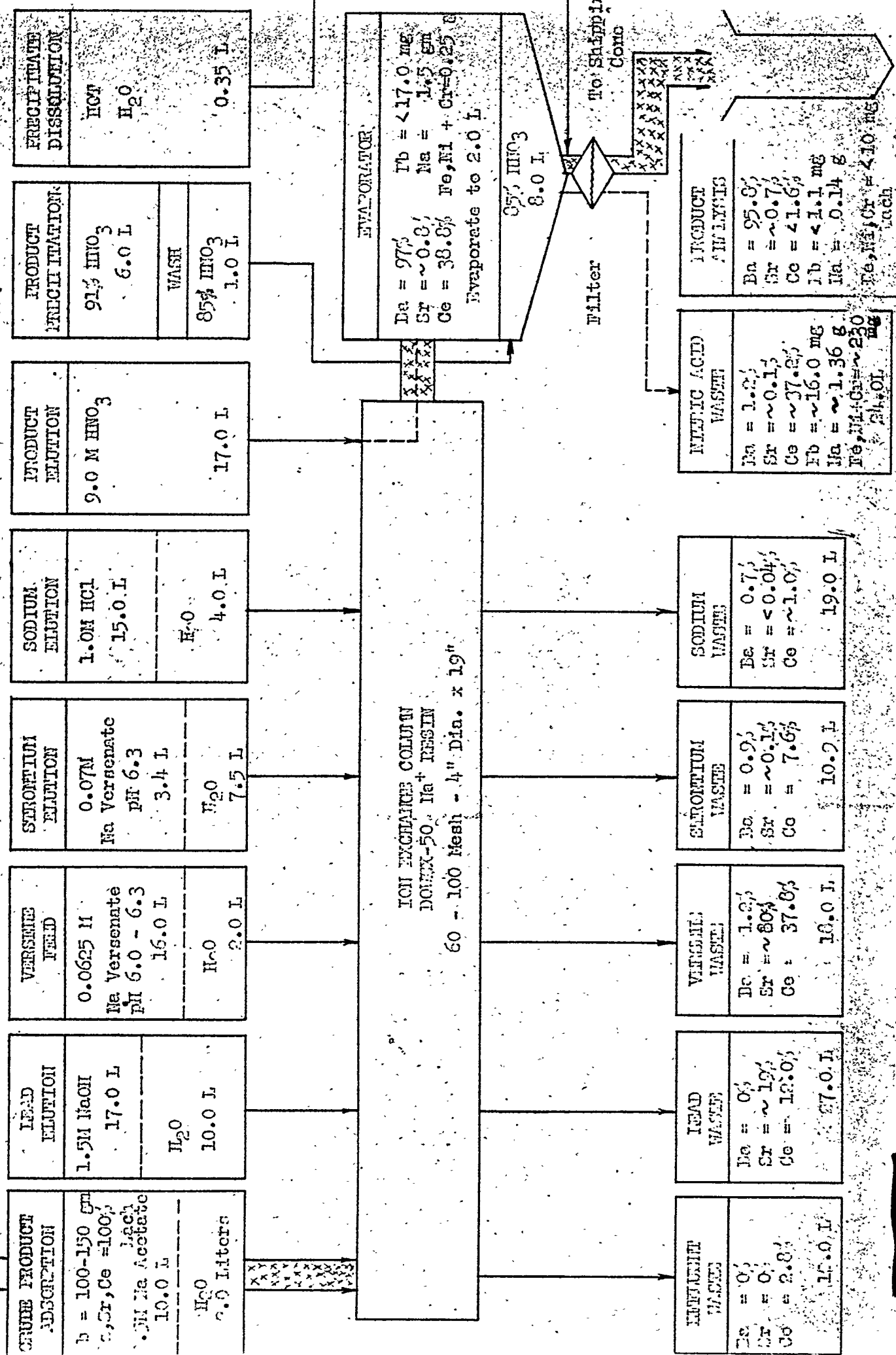
CONDITIONS: Approximately 20gm transverse sections of an MTR-Assembly were dissolved in $NaOH-NaNO_3$ solution.

KEY: Initial mole ratios are indicated as $Al:NaNO_3:NaOH$; Al molarity = final concentration.

ASSUMPTIONS: Final Solution: (1) Na^+ is the only cation.
(2) All anions are monovalent.
(3) Approximate total ionic strength $\cong (Na) \times 2$

EQUATIONS:
(1) $8\ Al + 3\ NaNO_3 + 5\ NaOH + 2\ H_2O \longrightarrow 8\ Na\ AlO_2 + 3\ NH_3$
(2) $2\ Al + 3\ NaNO_3 + 2\ NaOH \longrightarrow 3\ NaNO_2 + 2\ Na\ AlO_2 + H_2O.$

% Al DISSOLVED BY EQUATION (2)

FINAL RATIO (NO_2):(Al)

TOTAL IONIC STRENGTH — M

1:1.5:2
3.4 M Al

1:2:1
3.7 M Al

1:1:1
5.4 M Al

1:0.752:1
5.4 M Al

1:1:3.33
2.1 M Al

1:1.5:1
3.5 M Al

1:1:4.5
3.4 M Al

1:0.33:2
3.6 M Al

1:0.5:1
5.2 M Al

1:0.5:1.5
3.2 M Al

1:0.5:1
3.35 M Al

JEF

Figure 5

FLOWSHEET: MTR-RaLa PROCESS-Part 1
PREPARATION OF CRUDE BARIUM140 BY THE CAUSTIC-NITRATE PROCESS

DWG No1 2795

BASIS: 1 MTR Assembly

$$\left[\begin{array}{l} \text{1.63 Moles Aluminum} \\ \text{0.63 Moles Uranium} \\ 1.46\times10^{-2} \text{ Moles Ba} \end{array}\right]$$

ALUMINUM DISSOLUTION
5.0 M	NaOH
2.5 M	NaNO$_3$
5.0 M	Al
32 Liters	

NH$_3$

WASH
0.5 M NaOH
20.0 Liters.

2 HOURS

ALUMINUM WASTE
Barium	0.2 %
Uranium	0.3 %
Aluminum	99.7 %
52.0 Liters	

URANIUM DISSOLUTION
6.0 M HNO$_3$	5.0 Liters
WASH	
6.0 M HNO$_3$	5.0 Liters

PRODUCT PRECIPITANT
HNO$_3$
(90-92%)
8.0 Liters

PRODUCT PRECIPITATION
U+F.P.s	～99.7 %
Aluminum	～0.3 %
Evaporate to	2.0 Liters
85% HNO$_3$	
10.0 Liters	

3 HOURS

WASH
HNO$_3$
85% HNO$_3$
2.0 Liters

PRODUCT SOLVENT
0.5 M NaNO$_3$	3.0 Liters
WASH	
H$_2$O	7.0 Liters

2 HOURS

URANIUM WASTE
Barium	<0.1 %
Strontium	0.6 %
Cerium	95 %
Uranium	99.3 %
Aluminum	0.07 %
12.0 Liters	

CRUDE PRODUCT
Barium	99.6 %
Strontium	99.1 %
Cerium	4.7 %
Uranium	0.04 %
Aluminum	0.23 %
10.0 Liters	

TO ION EXCHANGE

Figure 6 - 21 -   Dwg. #12988

FLOWSHEET: LTR-RaLa PROCESS – PART II

Purification of Barium^{140} by the Versene Ion Exchange Process

CRUDE PRODUCT ABSORPTION

Al = 10.0 gm
Fe, Ni+Cr = ~1.5 gm
0.1M NaNO$_3$
0.02M HNO$_3$
Vol. = 10.0 L

H$_2$O
Vol. = 2.0 L

ALUMINUM ELUTION

1.5M NaOH
Vol. = 1.7 L

0.5M NaOH
Vol. = 7.7 L

H$_2$O
Vol. = 10.0 L

STRONTIUM ELUTION

0.07 M
Na Versenate
pH 6.3
Vol. = 12.0 L

H$_2$O
Vol. = 10.0 L

PRODUCT ELUTION

2.0M HNO$_3$
(Na Elution)
Vol. = 2.0 L

5.0M HNO$_3$
Vol. = 15.0 L

PRODUCT PRECIPITATION

90 – 95% HNO$_3$
Vol. = 8.0 L

WASH
85% HNO$_3$
Vol. = 1.0 L

PRECIPITATE DISSOLUTION

H$_2$O
Vol. = 0.50 L

ION EXCHANGE COLUMN

Dowex - 50 - NA$^+$ Resin
60 – 100 mesh   4" Dia. x 10"

EVAPORATOR

Ba = 96.5 %   Ce = 1.80%
Sr = <0.2%   Al = ~0.2 gm
NA = ~108 gm
Evaporate to 2.0 L
85% HNO$_3$
Vol. = 10.0 L

Filter

To Shipping Cone

PRODUCT ANALYSIS

Ba = 96%
Sr = <0.2%
Ce = ~0.07%
Al, Na, U,   } 10 mg ea.
Te, Ni, Cr)

NITRIC ACID WASTE

Ba = <0.5%
Sr = <0.007%
Ce = 1.73%
Al = ~190 mg
Na = ~108 gm
Vol. 9.0 L

STRONTIUM WASTE

Ba = 6.5%
Sr = 98.9%
Ce = 2.8%
Vol. = 22.8 L

ALUMINUM WASTE

Ba = ~0.1%
Sr = ~0.1%
Ce = ~0.1%
Al = 9.8 gm.
Vol. = 19.4 L

INFLUENT WASTE

Ba = <0.1%
Sr = <0.1%
Ce = <0.1%
Vol. = 12.0 L

FIGURE 7

SEPARATION OF $BaSO_4$ FROM U, Al AND FISSION PRODUCTS BY PRECIPITATION FROM 2.0 M H_2SO_4 AS A FUNCTION OF HNO_3 CONCENTRATION.

CONDITIONS:
Ba = 1.25×10^{-2} M   Al = 2.55×10^{-3} M
Sr = 1.96×10^{-2} M   U = 4.70×10^{-2} M
Ce = 2.45×10^{-3} M   Total Vol = 58.3 ml

FILTER: Medium Sintered Glass: 20 mm Dia.

FILTER AID: Anal. Celite; 12 gm/l; 1/4" precoat.

Digest 15min at B.P.; Cool 15min; Filter.

Curve labels within figure:
- Sr Carried by $BaSO_4$
- Al Carried by $BaSO_4$
- Ce Carried by $BaSO_4$
- Ba Loss in Filtrate
- U Carried by $BaSO_4$

Y-axis: PERCENT OF EACH CATION (0.001, 0.01, 0.10, 1.0, 10.0)

X-axis: NITRIC ACID NORMALITY (2.0, 4.0, 6.0, 8.0, 10.0, 12.0)

FIGURE 8

SEPARATION OF BaSO₄ FROM U, Al AND FISSION PRODUCTS BY PRECIPI-
TATION FROM AN HNO₃ – H₂SO₄ SYSTEM AS A FUNCTION OF TEMPERATURE
AND BARIUM CONCENTRATION

CONDITIONS: Mole Ratio of Ba, Sr, Ce = 0.728: 1.141: 0.143; Vol = 58.3 ml. 3.13 X10⁻³ M Ba ≃ 0.5 gm
Ba/M.T.R Assembly. 2.31 N HNO₃, 2.0 M H₂SO₄, 4.70 X10⁻² M U, 2.55X10⁻³ M Al;
digest 15 min at B.P.

FILTER: "M" Sintered Glass, 20 mm dia, FILTER AID: Anal. Celite, 12 gm/l; 1/4"precoat.

LEGEND: A: Filt. hot; add Celite after digest. C: Filt. hot; add Celite before digest.
B: " cold; " " " " D: " cold; " " " "

Sr carried by BaSO₄

Ce carried by BaSO₄

Ba loss in filtrate
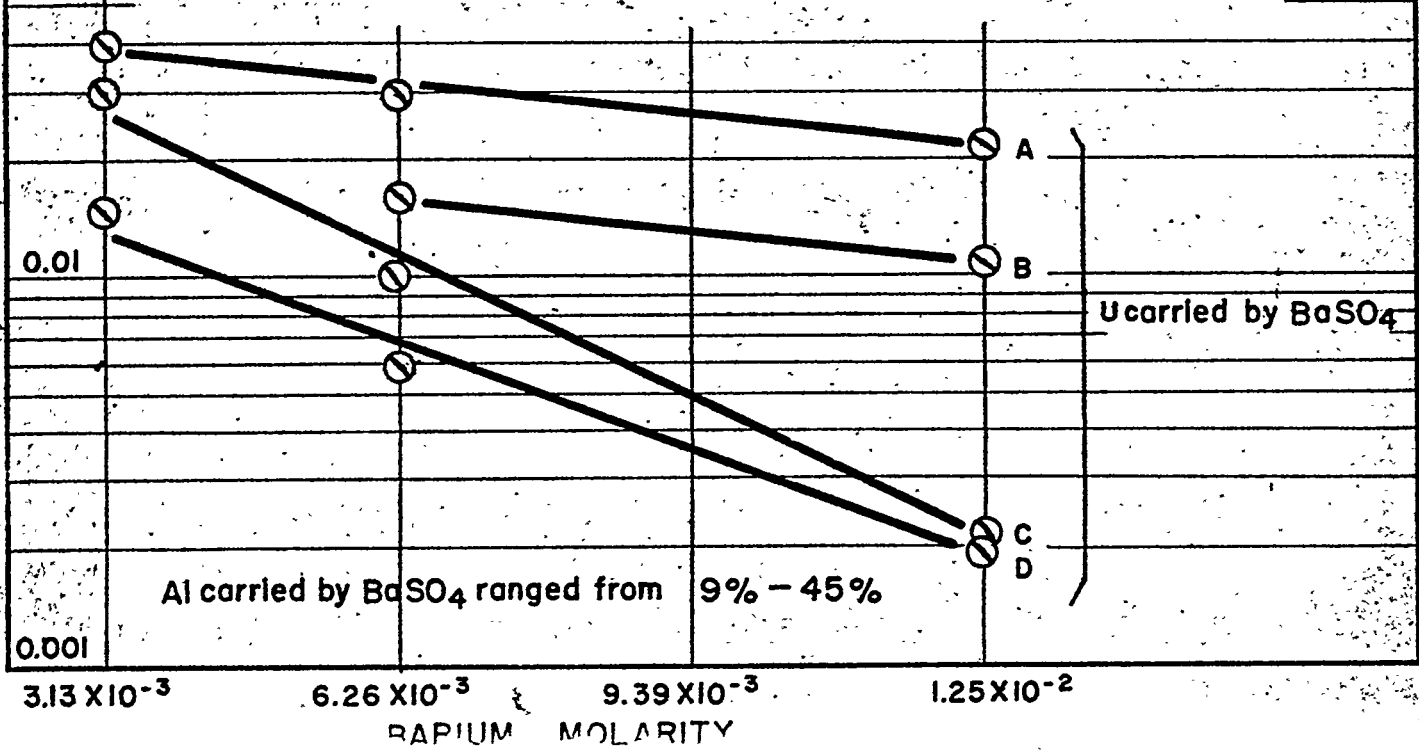
U carried by BaSO₄

Al carried by BaSO₄ ranged from 9% – 45%

PERCENT OF EACH CATION

10.0
1.0
0.10
0.01
0.001

3.13 X10⁻³   6.26 X10⁻³   9.39 X10⁻³   1.25 X10⁻²

BARIUM MOLARITY

FIGURE 9

SEPARATION OF BaSO$_4$ FROM U, Al AND FISSION PRODUCTS
BY PRECIPITATION FROM 2.3 N HNO$_3$ AS A FUNCTION OF
H$_2$SO$_4$ CONCENTRATION

CONDITIONS: Ba = 1.25×10^{-2} M   Al = 2.55×10^{-3} M
Sr = 1.96×10^{-2} M   U = 4.70×10^{-2} M
Ce = 2.45×10^{-3} M   Total Vol = 58.3 ml

FILTER: Medium Sintered Glass; 20 mm Dia.

FILTER AID: Anal. Celite; 12 gm/l; 1/4" precoat.

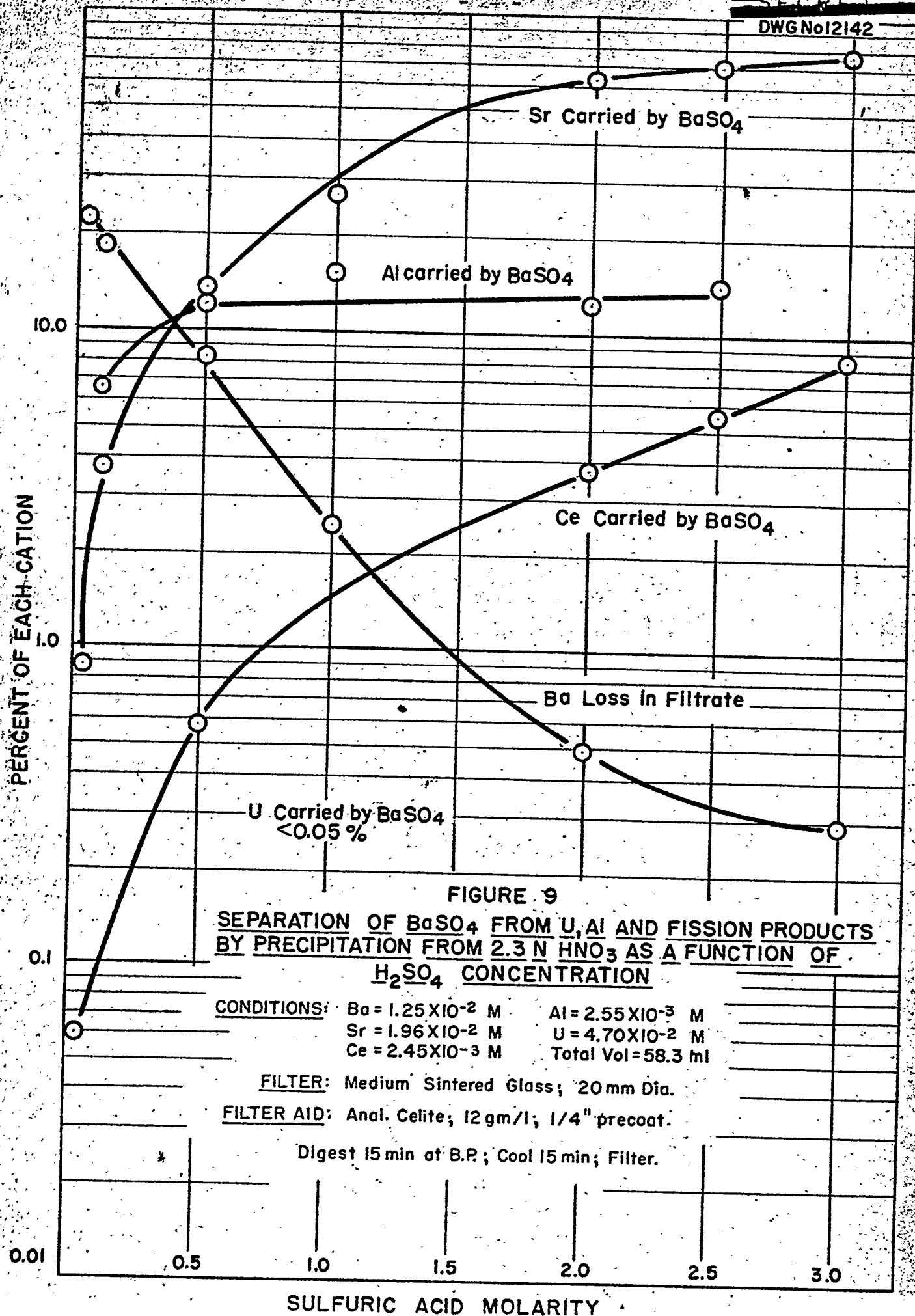Digest 15 min at B.P.; Cool 15 min; Filter.

SULFURIC ACID MOLARITY

Figure 10   - 25 -

ELUTION OF BARIUM FROM DOWEX-50 RESIN WITH NITRIC ACID

COLUMN: 2.3 cm x 53.7 cm
Dowex - 50 - H⁺ Resin
60 - 100 mesh

ADSORPTION: 10 mg Ba + Ba tracer / 50 ml 0.5 M HNO_3.

ELUTION: HNO_3 (concentration as shown)

FLOW RATE: 0.3 ∓ 0.2 ml / min / cm² column cross-section.

JH Pannell - RE Blanco
11-8-51

JEF